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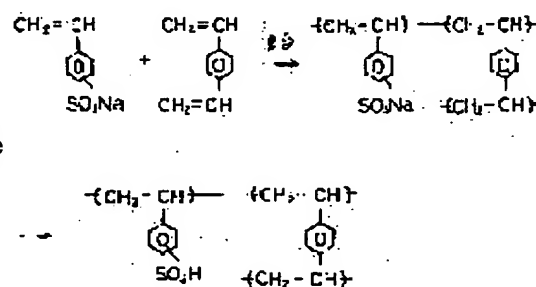
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**(54) GAS DIFFUSION ELECTRODE FOR SOLID POLYMER ELECTROLYTE MEMBRANE TYPE FUEL CELL AND ITS MANUFACTURING METHOD**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an electrode for solid polymer electrolyte membrane type fuel cells capable of enhancing the characteristics of the electrode by securing continuous proton conduction paths while securing more triphasic interfaces serving as electrode reaction sites, and resultantly capable of economically enhancing the output performance of a fuel cell incorporating this electrode.

**SOLUTION:** This gas diffusion electrode equipped with catalyst layers for sandwiching between them a solid polymer electrolyte membrane of the solid polymer electrolyte membrane type fuel cell is characterized in that the catalyst layers contain a compound made by introducing a proton-conductive functional group into a hydrocarbon resin.

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CLAIMS

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[Claim(s)]

[Claim 1] The gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed in the gas diffusion electrode equipped with the catalyst bed which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell.

[Claim 2] The manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of a process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed in the manufacture approach of the gas diffusion electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell, and a process which carries out the polymerization of this monomer and carries out macromolecule quantification.

[Claim 3] The manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of the process which sets to the manufacture approach of the electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell; and mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, a process which carries out the polymerization of this monomer and carries out macromolecule quantification, and a process to which a proton conductivity functional group is introduced into said macromolecule.

[Claim 4] Said proton conductivity functional group is the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being chosen from the acid radical which consists of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid, and its manufacture approach.

[Claim 5] Said hydrocarbon system resin Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, a polycarbonate, Polyethylene terephthalate, polyarylate, polysulfone, polyether sulphone, A polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, The gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being polymers which consist of carbon and hydrogen at least, such as a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, and its manufacture approach.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode for solid-state polyelectrolyte membrane type fuel cells, and its manufacture approach.

[0002]

[Description of the Prior Art] In order to cope with the environment and resource problem in earth scales, such as CO<sub>2</sub> effluent control for an air pollution control, and a petroleum-resources exhaustion, conventionally, it is clean and energy density is high, as for the solid-state polyelectrolyte mold fuel cell which the charging time makes unnecessary, it is most brought into the limelight, and researches and developments are furthered at a quick pace in each country in the world including Japan.

[0003] A polymer electrolyte fuel cell is equipment which acquires the electromotive force produced in that case by being characterized by having the solid-state polyelectrolyte film of proton conductivity as the component part, and making fuel gas and oxidation gas, such as hydrogen, react electrochemically.

[0004] The electrode reaction at the time of hydrogen gas being used for a fuel cell as fuel gas, and oxygen being used for it as oxidation gas is  $2H_2 \rightarrow 4H^{++} + 4e^-$  at an anode pole side. Reaction formula The proton which the reaction which becomes one occurred and was generated passes along the inside of a solid-electrolyte membrane, and is  $4H^{++} + O_2 + 4e^- \rightarrow 2H_2O$  in a cathode pole. Reaction formula The reaction which becomes two occurs and electromotive force arises among two poles.

[0005] By the way, at the present stage, some technical problems which must be conquered are still left behind to utilization of a fuel cell.

[0006] The presentation of a current electrode catalyst bed becomes carbon black from the ingredient and perfluorocarbon-sulfonic-acid system proton conductivity ingredient which supported the platinum which is a catalyst, the catalyst presentation which kneaded these is applied to base materials, such as carbon paper, and the gas diffusion electrode is formed as shown in a U.S. Pat. No. 4876115 number official report or JP,3-208260,A.

[0007] Being formed from the gas diffusion electrode which made the catalyst bed mixture of the styrene divinylbenzene sulfonic acid type resin which is the solid-state polyelectrolyte film at moreover, addition and the electrode characteristic of the ion-exchange resin to electrochemistry, 53, No.10, and the oxygen pole joined to a p812-817(1985) "solid-state polyelectrolyte (Nafion)", and the carbon powder which supported the catalyst metal, the styrene divinylbenzene sulfonic-acid-type-resin powder which is a proton conductor and a polystyrene binder is indicated.

[0008]

[Problem(s) to be Solved by the Invention] However, in a U.S. Pat. No. 4876115 number official report or JP,3-208260,A, if it must be made for the proton conductivity ingredient in the gas diffusion electrode of a fuel cell not to have to melt into water and there are many functional groups of proton conductivity, it will become water solubility, therefore since a perfluorocarbon-sulfonic-acid system proton conductivity ingredient cannot enlarge ion exchange capacity, the migration of a proton to an electrolyte membrane becomes rate-limiting, and it cannot take out sufficient current.

[0009] moreover, although ion exchange capacity can be make larger than a perfluorocarbon sulfonic acid system proton conductivity ingredient about electrochemistry, 53, No.10, and p812-817 (1985), since a proton conductor be a powder, the poor contact of a powder particle arise by the defect of a powder particle etc., the function cannot fully demonstrate, but so it become rate-limiting move [ of a proton ] it, even a solid-state polyelectrolyte film do not reach and a proton cannot take out sufficient current.

[0010] thus, the proton generated in the three-phase zone on a catalyst (a hydrogen gas phase, a catalyst

phase, conductive matter phase) since ion exchange capacity of a Prior art was not large in the proton conductor in a catalyst bed being a powder configuration -- up to the solid-state polyelectrolyte film -- proton conduction -- moving in the inside of the body becomes rate-limiting, consequently sufficient current cannot be taken out. Therefore, in order to raise the output engine performance of a fuel cell, it is necessary to raise the property of this proton conductor.

[0011] Although the platinum catalyst and the perfluorocarbon-sulfonic-acid system proton conduction ingredient are used for the catalyst bed of this basic presentation and it has become the factor of high cost, as for the platinum catalyst, the possibility of low-cost-izing with the technique of recycle and amount[ of low / used ]-izing is left behind.

[0012] however, perfluorocarbon-sulfonic-acid resin with a very expensive proton conduction ingredient -- base -- this is solution-ized in a raw material and it is manufactured. It is an ingredient expensive as much as platinum, and that cost is used as an ingredient of each development manufacturer company mainstream of a fuel cell stack and a gas diffusion electrode current [ many ], and low-cost-izing of a fuel cell is difficult for it as [ this ]. Therefore, a proton conductor needs to be low-cost-ized.

[0013] this invention offers the electrode for solid-state polyelectrolyte membrane type fuel cells and fuel cell which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it in order to secure a continuous proton tract, securing more three-phase zones which are what solved the above-mentioned technical problem, and are electrode reaction sites.

[0014]

[Means for Solving the Problem] Invention of claim 1 made in order to solve the above-mentioned technical technical problem is a gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed in the gas diffusion electrode equipped with the catalyst bed which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell.

[0015] it is possible to offer the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it by invention of claim 1 since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites.

[0016] Invention of claim 2 made in order to solve the above-mentioned technical technical problem be the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterize by to consist of a process which mix and distribute the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed , and a process which carry out the polymerization of this monomer and carry out macromolecule quantification in the manufacture approach of the gas diffusion electrode which pinch the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell .

[0017] it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it by invention of claim 2 since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites.

[0018] Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0019] Invention of claim 3 made in order to solve the above-mentioned technical technical problem sets to the manufacture approach of the electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane-type fuel cell, and is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane-type fuel cells which consists of the process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, a process which carries out the polymerization of this monomer and carries out macromolecule quantification, and a process to which a proton conductivity functional group is introduced into said macromolecule.

[0020] Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0021] Invention of claim 4 made in order to solve the above-mentioned technical technical problem is the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by choosing said proton conductivity functional group from the acid radical which consists of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid, and its manufacture approach.

[0022] By invention of claim 4, the effectiveness of making proton conductivity discover can be offered.

[0023] Invention of claim 5 made in order to solve the above-mentioned technical technical problem Said hydrocarbon system resin Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, a polycarbonate, Polyethylene terephthalate, polyarylate, polysulfone, polyether sulphone, A polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, They are the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being polymers which consist of carbon and hydrogen at least, such as a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, and its manufacture approach.

[0024] The effectiveness that a polymer can be made from a monomer and a proton conductivity functional group can be introduced by invention of claim 5 can be offered.

[0025]

[Embodiment of the Invention] Hereafter, this invention is explained with reference to a drawing.

[0026] After this invention mixes and distributes the monomer of the compound which introduced the proton conductivity functional group into the hydrocarbon system resin which is a proton conductor at a catalyst bed, its property of an electrode improves by carry out the polymerization of the monomer, carry out macromolecule quantification and produce in the catalyst bed of the gas diffusion electrode for polymer electrolyte fuel cells which consists of polytetrafluoroethylene which is a repellent a catalyst support carbon particle, proton conductivity material, or if needed in order to secure a continuous proton tract, secure more three-phase zones which are electrode reaction sites. it is invention which can boil markedly the output engine performance of the fuel cell combined with this electrode as a result, and can raise it.

[0027] This gas diffusion electrode is a gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed.

[0028] In the manufacture approach of the gas diffusion electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell, the manufacture approach of the manufacture approach of the gas diffusion electrode is carried out from the process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed, and the process which carries out the polymerization of this monomer and carries out macromolecule quantification.

[0029] Moreover, as other manufacture approaches, the manufacture approach is carried out from the process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, the process which carries out the polymerization of this monomer and carries out macromolecule quantification, and the process to which a proton conductivity functional group is introduced into said macromolecule.

[0030] Here, the acid radical which consists of that of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid is introduced as a proton conductivity functional group. Among these, it is desirable to make a sulfonic group into an indispensable functional group. because, as hydrocarbon system resin used for the proton conductor which is because it has the effectiveness of the dissociation constant of a proton being high and having high proton conductivity Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, A polycarbonate, polyethylene terephthalate, polyarylate, Polymers, such as polysulfone, polyether sulphone, a polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, are mentioned.

[0031] There is especially no limit in the approach of introducing this functional group into hydrocarbon system resin. It is better to compound the resin which introduces a functional group and has a functional group, after carrying out the polymerization of the monomer and making it macromolecule resin like the reaction formula of drawing 4, but to compound the macromolecule resin which has a functional group by carrying out a polymerization like [ it is desirable and ] the reaction formula of drawing 3, after introducing a functional group into a resin monomer.

[0032] The reason is that it is easier to introduce into a monomer rather than it introduces a functional group into a polymer.

[0033] There is especially no limit about the approach of making this proton conductor forming into a catalyst bed. After mixing and distributing a resin monomer in catalyst bed components, such as a catalyst support carbon particle, and coating a resin monomer on the catalyst bed which the catalyst bed was formed, and carried out the polymerization of the monomer, carried out giant-molecule quantification or was formed, the polymerization of the monomer may be carried out and giant-molecule quantification may be carried out.

[0034] (Example 1) As shown in drawing 1 (a), the dispersion undiluted solution (Daikin Industries, LTD.,

- POLYFLOND1 grade) whose poly TERORA fluoro ethylene (PTFE) particle content concentration is 60% was diluted with water so that PTFE concentration might become 15% of the weight. Carbon paper CP with a thickness of 180 micrometers (the Toray Industries, Inc. make, TGP-060) was dipped into this solution. [0035] Then, the above-mentioned carbon paper CP was picked out from the solution, in 80-degree-C atmospheric air, after desiccation ( drawing 1 (b) ), it held for 390 degree-Cx 60 minutes, PTFE was sintered ( drawing 1 (c) ), and the carbon paper given a water-repellent finish was obtained ( drawing 1 R> 1 (d) ). [0036] As shown in drawing 2 , platinum concentration carried out homogeneity distribution of the platinum support carbon (product [ made from Johnson MASSEI ], HISPEC4000) 15g which is 40 % of the weight into methanol 115g and 115g of water. [0037] Subsequently, 10g [ of sodium styrenesulfonate ] and divinylbenzene (DVB) 1g and azobisisobutyronitril (ABIN) 0.1g were added into this solution, it mixed and distributed, and the catalyst paste was obtained ( drawing 2 ). In addition, the above-mentioned reaction formula is expressed with the reaction shown in drawing 3 . [0038] The catalyst bed was formed so that the amount of platinum support might become 0.2 mg/cm<sup>2</sup> to water-repellent-finish carbon paper with a doctor blade method about this catalyst paste. Then, after the air dried, it held for 80 degree-Cx 8 hours, and the polymerization of the monomer was carried out. Next, after washing several times with water, it dipped in the sulfuric-acid water solution of 0.5 mol/l, the sulfonic group was exchanged for H mold, and the gas diffusion electrode was obtained ( drawing 1 (e) ). [0039] The polyelectrolyte film compounded and obtained by the approach of the following [ this gas diffusion electrode ] was inserted, 8 MPa, the heat press was carried out for 5 minutes, and 150 degrees C of membrane electrode zygotes were produced. [0040] After irradiating the gamma ray of 20kG(ies) in nitrogen and under ordinary temperature at the Pori (ethylene tetrafluoroethylene) film of 50 micrometers of thickness, the graft of the styrene chain was carried out to Pori (ethylene tetrafluoroethylene) by dipping a film at 60 degrees C into the mixed solution of styrene monomer:divinylbenzene:xylene=95:5:30 (volume section) for 2 hours. 50 degrees C was dipped after drying a film for 1 hour during mixing of the chlorosulfonic acid 30 volume section and the 1 and 2-dichloroethane 100 volume section. The film after desiccation was washed by 90-degree C new deionized water for 2 hours. The chemical formula (polystyrene sulfonate graft-Pori (ethylene-TETORO fluoro ethylene)) of the film is shown in drawing 7 . [0041] Next, this membrane electrode zygote was attached to the fuel cell single cel, and generation-of-electrical-energy evaluation was carried out. Evaluation conditions used air as the cel temperature of 75 degrees C, and oxidizer gas, and used pure hydrogen as fuel gas, and these utilization factors supplied both gas pressure by 0.25MPa(s) 40% and 80% respectively. Under the present circumstances, in oxidizer gas, the steam of 0.22 was supplied and humidified by the mole ratio to hydrogen capacity at 0.04 and fuel gas to the air content by the mole ratio. The evaluation result is shown in drawing 5 R> 5 . [0042] (Example 2) The catalyst bed was formed so that it might become the amount of platinum of an example 1 and the amount same by the same approach at the same water-repellent-finish carbon paper as an example 1 about the catalyst paste which carried out homogeneity distribution of the same platinum support carbon 15g as an example 1 into isopropyl alcohol 115g and 115g of water. [0043] Then, spreading and desiccation were repeated in several steps on the catalyst bed front face in which the solution which added 10g [ of sodium styrenesulfonate ] and divinylbenzene 1g and azobisisobutyronitril 0.1g into methanol 100g, and was mixed and distributed was formed on water-repellent-finish carbon paper. Then, it held for 80 degree-Cx 8 hours, the polymerization of the monomer was carried out, and the gas diffusion electrode was obtained. [0044] The membrane electrode zygote was produced on the same conditions as an example 1, and generation-of-electrical-energy evaluation of the same electrolyte membrane as an example 1 and the above-mentioned electrode was carried out on the same evaluation conditions as an example 1. The evaluation result is shown in drawing 5 . [0045] (Example of a comparison) Homogeneity distribution of the same platinum support carbon 15g as an example 1 and the 180g (the Asahi Chemical Co., Ltd. make, SS-1080) of 5% of the weight of the ion-exchange-resin solutions was carried out into isopropyl alcohol 24g and 24g of water, and the catalyst paste was obtained. The catalyst bed was formed in the same water-repellent-finish carbon paper as an example 1 so that it might become the amount of platinum of an example 1 and the amount same by the same approach, and the gas diffusion electrode was obtained. In addition, the chemical formula of the above-mentioned ion exchange resin consists of a chemical formula shown in drawing 6 . [0046] Nafion112 (product made from Du Pont) was used for the macromolecule electrolysis film, 2 MPa,



the heat press was carried out for 5 minutes, the membrane electrode zygote was produced, and 120 degrees C carried out generation-of-electrical-energy evaluation on the same evaluation conditions as an example 1. The evaluation result is shown in drawing 5.

[0047] drawing 5 is a graph showing the relation between output voltage and current density, and is understood from this graph -- as -- an example 1 and an example 2 -- in all, as compared with the example of a comparison, output voltage is high. it is thought that this reason boils markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode in order to secure a continuous proton tract, securing more three-phase zones which are electrode reaction sites, and raises it.

[0048]

[Effect of the Invention] In the gas diffusion electrode equipped with the catalyst bed to which invention of the 1st of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell Since it is the gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites, the property of an electrode can be improved. By consequently, low cost it is possible to offer the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it.

[0049] In the manufacture approach of a gas diffusion electrode that furthermore invention of the 2nd of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell The process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed, Since it is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by carrying out the polymerization of this monomer and consisting of a process which carries out macromolecule quantification Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites, the property of an electrode can be improved. By consequently, low cost it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it. Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0050] In the manufacture approach of an electrode that furthermore invention of the 3rd of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell The process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, and the process which carries out the polymerization of this monomer and carries out macromolecule quantification, Since it is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of a process to which a proton conductivity functional group is introduced into said macromolecule Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites like the 2nd above-mentioned invention, the property of an electrode can be improved. By consequently, low cost it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it. Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

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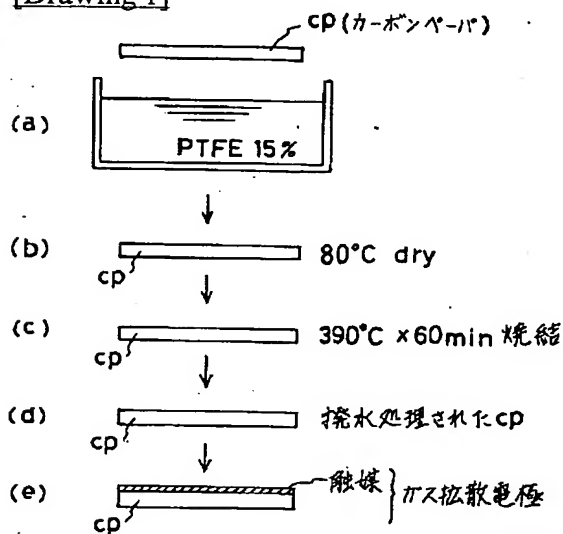
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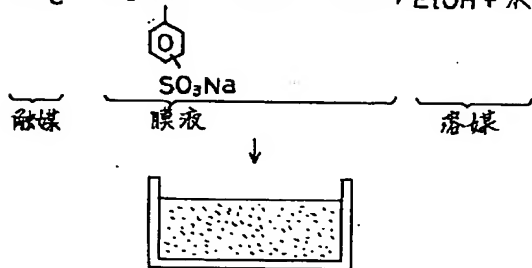
## DRAWINGS

[Drawing 1]

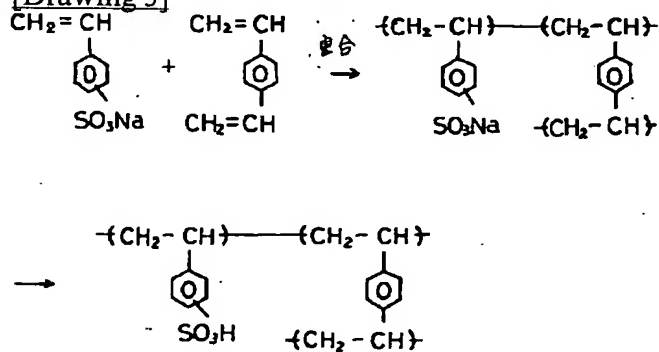


[Drawing 2]

Pt/C + CH<sub>2</sub>=CH + DVB + ABIN/EtOH + 水

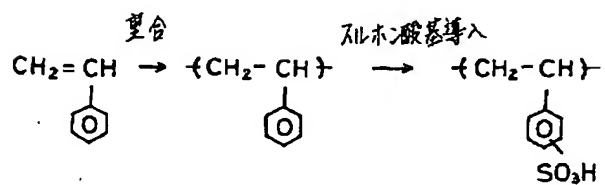


[Drawing 3]

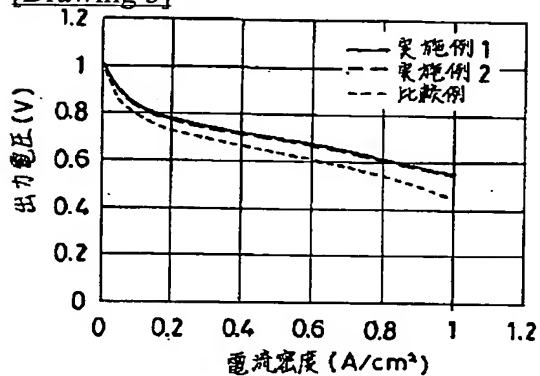


[Drawing 4]

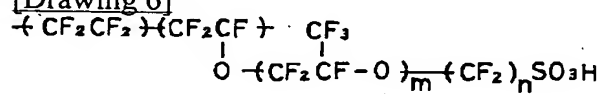




[Drawing 5]

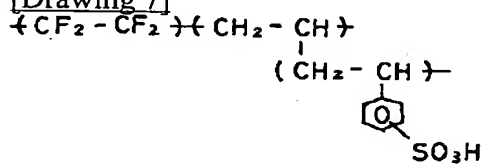


[Drawing 6]



$$\begin{aligned} m &= 0 \text{ or } 1 \\ n &= 2 \sim 5 \\ x &= 15 \sim 14 \end{aligned}$$

[Drawing 7]



[Translation done.]





